

12

EUROPEAN PATENT APPLICATION

21 Application number: 85200407.6

51 Int. Cl.⁴: C 10 L 9/08

22 Date of filing: 18.03.85

30 Priority: 11.04.84 GB 8409402

43 Date of publication of application:
18.10.85 Bulletin 85/42

84 Designated Contracting States:
AT BE CH DE FR GB IT LI NL

71 Applicant: SHELL INTERNATIONALE RESEARCH
MAATSCHAPPIJ B.V.
Carel van Bylandtlaan 30
NL-2596 HR Den Haag(NL)

72 Inventor: Lindhout, Izaak
Carel van Bylandtlaan 30
NL-2596 HR The Hague(NL)

72 Inventor: Geiger, Ferdinand Johan Adriaan
Carel van Bylandtlaan 30
NL-2596 HR The Hague(NL)

72 Inventor: Alberts, Barend
Carel van Bylandtlaan 30
NL-2596 HR The Hague(NL)

72 Inventor: Downing, Roger Stewart
Badhuisweg 3
NL-1031 CM The Hague(NL)

74 Representative: Aalbers, Onno et al,
P.O. Box 302
NL-2501 CH The Hague(NL)

54 A process for calcining green coke.

57 A process for calcining green coke containing combustible volatile matter in at least two stages, whereby in a first stage the green coke is heated in a furnace to a temperature of between 750°C and 1000°C and in a second stage in a second furnace to a temperature of between 1200°C and 1600°C, characterized in that the heating in the first stage is carried out with a controlled heat-up rate of less than 60°C/min in the temperature range of between 600°C and 800°C, whereby said heating up is achieved by hot combusted volatile matter, which is obtained by withdrawing the released volatile matter from the first stage, burning said volatile matter outside the first stage and recycling the burnt volatile matter to the first stage.

A PROCESS FOR CALCINING GREEN COKE

The invention relates to a process for calcining green coke containing combustible volatile matter in at least two stages, whereby in a first stage the green coke is heated in a furnace to a temperature of between 750 °C and 1000 °C and in a second stage in a second furnace to a temperature of between 1200 °C and 1600 °C.

It is generally known that green coke made from a suitable hydrocarbon feedstock may be converted to high quality needle coke for use in high performance graphite electrodes which are applied in electric ore furnaces, or other purposes, like in baked carbon anodes in aluminium cells. For this purpose the green coke, after the water being removed at relatively low temperatures, is heated (precalcinated) in a furnace to a temperature which necessary to release at least a part of the combustible volatile matter, generally around 800 °C. In a further stage the coke is calcined in a second furnace to a temperature in the range between 1200 °C and 1600 °C. In principle in each of the stages either a shaft kiln, a rotary kiln or a rotary hearth furnace may be used, depending on the specific circumstances. After the precalcination cooling of the product may optionally take place, before the second stage calcination is carried out. The patent literature describes a number of processes for calcining coke, for example UK patent specification 1,603,924, UK patent applications 2,093,061 and 2,016,512, German patent specification 2,931,475 and US patent specification 4,291,008.

In UK patent specification 1,603,924 is disclosed a process for calcining green coke in three stages of heating furnaces which are connected in series and in which process in a first step the water is evaporated from the green coke, in a second step the volatile matter is distilled off and burnt from the dried coke and

in a third step the coke is calcined. In the precalcination stage preheated air is introduced into the burning kiln in order to burn the released volatile matter. Disadvantages are the degradation in particle size distribution upon calcination, the high friability of the product obtained by such a process and the lower product yield resulting from coke combustion.

Applicant has now found a process in which these disadvantages may be avoided.

The invention relates to a process for calcining green coke containing combustible volatile matter in at least two stages, whereby in a first stage the green coke is heated in a furnace to a temperature of between 750 °C and 1000 °C and in a second stage in a second furnace to a temperature of between 1200 °C and 1600 °C, characterized in that the heating in the first stage is carried out with a controlled heat-up rate of less than 60 °C/min in the temperature range of between 600 °C and 800 °C, whereby said heating up is achieved by hot combusted volatile matter, which is obtained by withdrawing the released volatile matter from the first stage, burning said volatile matter outside the first stage and recycling the burnt volatile matter to the first stage. Part of the hot combusted gases may be obtained by burning an additional combustible gas outside the first stage and introducing the burnt gas into the first stage.

A major advantage of the process according to the invention is that the calcined coke contains sufficient coarse material, which makes it especially suitable for the manufacture of ultra high power electrodes.

It is advantageous to carry out the first stage, namely the precalcination in a non-oxidizing atmosphere, this means that except from some oxygen leaked into the kiln because it works below atmospheric pressure, there is no more or hardly any free oxygen present in the recycled gases. The atmosphere in the precalcination stage could also be described as reducing.

In principle in the first stage any type of furnace is suitable, a rotary kiln is preferred. In the second stage any type of kiln may be suitable. Preference is given to the combination of a rotary kiln with a rotary hearth furnace in the first and second stage respectively.

The heat-up rate control in the first stage is regulated by the temperature and the amount of combusted gases, which preferably flow countercurrently with the direction in which the green coke flows. In a rotary kiln the direction in which the green coke flows, has a small angle with the horizontal surface. The inclination of said rotary kiln is generally below 5°. Depending upon the total length and the rotational speed of the kiln the retention time of the coke in the first kiln may be so chosen that the heat-up rate does not exceed 60 °C per minute, preferably the heat-up rate is less than 40 °C per minute. At the upper part of the rotary kiln the green coke is introduced and due to the rotation of the kiln and the gravity the green coke moves to the lower end of the kiln. The combustible volatile matter released from the green coke in the first stage, leaves the upper end and is recycled via a burner to the first stage furnace. Additional combustible gas if necessary, and air are added, so that combustion takes place in the burner. The combusted gases entering the lower part of the kiln have a temperature of between 900 °C and 1300 °C. A part of the combustible volatile matter is withdrawn from the recycling system before entering the burner. The right temperature and the amount of burnt gas necessary to achieve the controlled release of the combustible gases from the green coke is in this way secured. The amount of oxygen in the air introduced into the burner, is generally completely used for combustion of the gases, before these are recycled to the furnace in the first stage. The precalcined coke leaving the lower part of the kiln is transported to a rotary hearth furnace or other kiln. The kilns of the first and the second stage may be so arranged that the transport takes place by gravity. The inlet of the

calciner may be positioned immediately below the outlet of the precalciner and the precalcined coke is directly dropped into the coke feeding device of the calciner. Transportation may also take place by means of a conveyor. After the green coke has been
5 subjected to precalcination, the obtained product may preferably be cooled to a temperature below 100 °C, or even to room temperature. As already stated hereinbefore the second stage (calcination) may take place in any kind of furnace, in which the presence of free oxygen may be tolerated. Preference is given to a
10 rotary hearth furnace, which is well known in industry.

The process as applicable to any type of green coke, produced by delayed coking from heavy oils of petroleum or coal origin, such as residue oils of catalytic cracking, thermal cracking or steam cracking, straight run oils and tars resulting from thermal
15 cracking or coal tar pitch or any suitable blend of two or more of the above-mentioned oils before or after any additional treatment as thermal treatment, solvent extraction or hydrotreatment and the like.

Furthermore the process according to the invention may be
20 carried out in such a way that only one furnace is used with two different stages: the precalcination and the calcination, wherein the temperatures and gas compositions are controlled.

EXAMPLE

Green coke with a water content of 9% weight was introduced
25 at the upper end into a rotary kiln (with a length of 12 metres and an internal diameter of 0.5 metre) and precalcined to a temperature of 826 °C. The green coke was introduced at a rate of 250 kg/h, while the kiln was operated at 2 rpm (rotations per minute), the inclination being 2.5 degrees. The green coke was
30 obtained as residue in the steam cracking process of naphtha and gas oil.

The green coke was heated-up with a flue gas which had a temperature of 950 °C and which gas flowed in the direction countercurrently with the direction in which the coke was moving.
35 The outlet temperature of the flue gas was 480 °C. The flue gas

which contained no free oxygen, was produced by external stoichiometric combustion in a burner chamber of 16 kg/h natural gas with 206 kg/h air of ambient temperature and quenching the adiabatic flame temperature with a recycle of 730 kg/h of the total amount of 1081 kg/h of kiln-off gas. 357 kg/h of the kiln-off gas is withdrawn from the recycle stream. 218 kg/h of precalcined coke was obtained at the lower end of the rotary kiln.

The heat-up rate of the coke in the temperature range of from 600 °C to 800 °C was 24 °C/min.

After cooling to 20 °C precalcined coke was introduced at a rate of 100 kg/h at the upper end into a second rotary kiln with a final temperature of 1380 °C. This rotary kiln was operated at 3.6 rpm and had the same length and diameter as the first kiln. The inclination was 2.5 degrees. The coke was heated up by once through countercurrent heat exchange in an oxidizing atmosphere with a flue gas which had an inlet temperature of 1480 °C. The flue gas was obtained by combustion of natural gas with air and additional air was added to maintain an oxidizing atmosphere in the kiln. Starting from 100 kg/h of precalcined coke 94 kg/h of calcined coke was obtained. Real density was 2.13 g/ml.

Comparative example

A comparative experiment was carried out in the same rotary kilns, in which the precalcination and the final calcination took place.

250 kg/h of green coke was introduced at the upper end into a rotary kiln and precalcinated, while the kiln was operated at 2 rpm.

The green coke was heated-up with a flue gas which had a temperature of 950 °C and which gas flowed in the same direction as the coke was moving in the kiln. The flue gas was obtained by burning 17 kg of natural gas with 221 kg/h air of ambient temperature and was quenched with 312 kg/h additional air of ambient temperature. Burning of the released combustible gases took place in the rotary kiln. No recycle of the flue gas took place. 214 kg/h of precalcined coke was obtained.

The heat-up rate of the coke in the temperature range of from 600 ° to 800 °C could not be controlled, when additional air was used.

5 The precalcined coke was calcined in the second rotary kiln under exactly the same conditions as described in the example. Starting from 100 kg/h of precalcined coke 94 kg/h of calcined coke was obtained. Real density was 2.13 g/ml.

10 The calcined cokes obtained by the process according to the invention (example) and the process according to the comparative example differed considerably in physical characteristics.

Hereinafter the friability of the calcined cokes will be compared.

TABLE 1

coke particle size distribution	Green coke	Calcined coke	
		obtained by process acc. to invention	obtained by process acc. to comparative experiment
fraction < 1 mm	22%w	25%w	27%w
fraction < 5.6 mm	40%w	42%w	52%w
fraction < 10 mm	55%w	59%w	69%w

TABLE 2

Breakdown of coke fraction 8 to 9.5 mm in friability test *	Green coke	Calcined coke	
		obtained by process acc. to invention	obtained by process acc. to comparative experiment
fraction < 1 mm (formed)	20%w	20%w	23%w
fraction < 5.6 mm (formed)	26%w	28%w	48%w
fraction < 8 mm (unchanged)	35%w	31%w	12%w

* In the friability test the coke fraction of 8 to 9.5 mm is subjected during one hour to mechanical action of 2400 rotations (40 rpm) in a rotating drum provided at the inner side with one baffle.

TABLE 3

	Calcined coke	
	obtained by process acc. to invention $\times 10^{-6} . K^{-1}$	obtained by process acc. to comparative example $\times 10^{-6} . K^{-1}$
Coefficient of thermal expansion for 20 mm \emptyset artefact. Artefact made by mixing and extrusion of calcined coke flour with coal tar binder pitch, baking of rod at 850 °C and graphitization of baked rod at 3000 °C Artefacts tested over a temperature range of 35 °C to 235 °C.	0.54	0.58

From table 1 it is evident that the friability of the cal-
cined coke produced by the process according to the invention has
been decreased, the coke has thus become less friable. Starting
from a green coke with a given size distribution, it is observed
5 that the obtained coke has hardly undergone any changes in size
distribution in the process according to the invention.

From table 2 it is evident that the calcined coke obtained
by the process according to the invention is better proof against
deterioration than the calcined coke not produced according to
10 the invention.

From table 3 it is evident that the calcined coke, when
graphitized, and prepared by the method according to our
invention, has a coefficient of thermal expansion which is less
than that of calcined and graphitized coke not prepared according
15 to the invention.

C L A I M S

1. A process for calcining green coke containing combustible volatile matter in at least two stages, whereby in a first stage the green coke is heated in a furnace to a temperature of between 750 °C and 1000 °C and in a second stage in a second furnace to a temperature of between 1200 °C and 1600 °C, characterized in that the heating in the first stage is carried out with a controlled heat-up rate of less than 60 °C/min in the temperature range of between 600 °C and 800 °C, whereby said heating up is achieved by hot combusted volatile matter, which is obtained by withdrawing the released volatile matter from the first stage, burning said volatile matter outside the first stage and recycling the burnt volatile matter to the first stage.
2. A process as claimed in claim 1, characterized in that part of the hot combusted volatile matter is obtained by burning an additional combustible gas outside the first stage and introducing the burnt gas into the first stage.
3. A process as claimed in claims 1-2, characterized in that in the first stage furnace a non-oxidizing atmosphere is upheld.
4. A process as claimed in claims 1-3, characterized in that in the first stage a rotary kiln is used.
5. A process as claimed in claims 1-4, characterized in that in the second stage a rotary hearth furnace is used.
6. A process as claimed in claims 1-4, characterized in that in the first stage the hot combusted volatile matter is recycled countercurrently with the direction in which the green coke, being precalcined, flows.
7. A process as claimed in claims 1-4 and 6, characterized in that the hot combusted volatile matter has a temperature of between 900 °C and 1300 °C.
8. A process as claimed in claims 1-4, 6 and 7, characterized in that the amount of oxygen is completely used for combustion of the combustible volatile matter derived from the coke and the

additional combustible gas, before they are recycled to rotary kiln.

- 5 9. A process as claimed in claims 4-5, characterized in that the rotary kiln is situated above the rotary hearth furnace, enabling the coke transport taking place by gravity.

10. A process as claimed in claims 1-9, characterized in that in the first stage the heating is carried out with a controlled heat-up rate of less than 40 °C/min.

- 10 11. A process as claimed in claims 1-10, characterized in that the precalcinated coke is cooled to a temperature below 100 °C, before it is subjected to the calcination in the second stage.